Thermally Conductive Carbon Filled Nylon 6,6

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Increasing the thermal conductivity of typically insulating polymers, such as nyion 6,6, opens new markets. A thermally conductive resin can be used for heat sink applications. This research focused on performing compounding runs followed by injection molding and through-plane thermal conductivity testing of carbon filled uylon 6,6 based resins. The three carbon fillers investigated included an electrically conductive carbon black, synthetic graphite particles, and a surface treated polyacrylonitrile (PAN) based carbon fiber. Conductive resins were produced and tested that contained varying amounts of these single carbon fillers. In addition, combinations of fillers were investigated by conducting a full 23 factorial design and a complete replicate. The objective of this paper was to determine the effects and interactions of each filler on the thermal conductivity of the resins. Synthetic graphite particles caused the largest increase in composite thermal conductivity. In addition, all the single fillers and combinations of fillers caused a statistically significant (at the 95% confidence level) increase in composite thermal conductivity. Polym. Compos. 25:186–193, 2004. © 2004 Secrety of Piastics Engineers.

INTRODUCTION

Loreasing the thermal conductivity of these resins opens large new markets. The advantages of conductive resins as compared to metals (typically used) include improved corrosion resistance, lighter weight, and the ability to adapt the conductivity properties to suit the application needs. For example, a thermally conductive resin is ideally suited for heat sink applications, such as lighting ballasts and transformer housings.

Typical thermal conductivity (TC) values for seme common materials are 0.2 to 0.3 for polymers, 234 for aluminum, 400 for copper, and 600 for graphite (all values in W/m·K). One approach to improving the thermal conductivity of a polymer is through the addition of a conductive filler material, such as carbon and metal. Conductive resins with a thermal conductivity from approximately 1 to 30 W/m·K can be used in heat sink applications (1).

A significant amount of work has been conducted varying the amount of single conductive fillers in a composite material (2-9). For example, ceramic fibers/particles (boron nitride, aluminum nitride, aluminum oxide), metal fibers/particles (aluminum, steel, iron, copper, silver) and Ni-coated glass fibers have been used (1, 3, 10-12). Metallic fillers have several disadvantages.

relative to carbon, which include higher density and greater susceptibility to exidation. Various types of carbons have been effective conductive fillers. For example, adding synthetic graphite to mylon 6.6 increases the thermal conductivity from approximately 0.3 W/m·K to 1 W/m·K (8). Carbon black and carbon fiber have also been used (1, 7, 9, 13-20). Carbon black fillers have been successfully used to improve electrical conductivity, but these materials often have relatively low thermal conductivity. Carbon fibers, on the other hand, improve both the thermal and electrical conductivities.

Taipalus et al. have studied the electrical conductivity of carbon fiber reinforced polypropylene/polyaniline complex blends (21). Limited work has concerned the effect of combinations of various types of conductive fillers, such as carbon black, synthetic graphite, and carbon fiber on the composite conductivity. Thongruang et al. have investigated the electrical conductivity and mechanical properties of composites containing both graphite and carbon fiber in high density polyethylene and ultrahigh molecular weight polyethylene (22). Other researchers have studied the synergistic effects of carbon black, synthetic graphite particles, and a milied pitch based carbon fiber in mylon 6,6 and polycarbonate on the thermal and electrical conductivity and shielding effectiveness (23–25).

In this project, researchers performed compounding runs followed by injection molding carbon filled nylon 6,6 test specimens. Material characterization tests included through-plane thermal conductivity, and optical

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microscopy to determine aspect ratio and orientation angle of the conductive fillers. The three carbon fillers investigated were Akzo Nobel's Ketjenblack EC-600 JD, Conoco's Thermocarb™ TC-300 Specialty Graphite, and Akzo Nobel's Fortafil 243 polyacrylonitrile (PAN) based carbon fiber. A total of 31 nylon 6,6 based formulations were produced and tested that contained varying amounts of these carbon fillers. These formulations included increasing amounts of a single carbon filler, as well as a 2³ factorial design. The goal of this project was to determine the effects of each filler and combinations of different fillers on the thermal conductivity of the conductive resins.

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MATERIALS AND EXPERIMENTAL METHODS Materials

The matrix used was DuPont Zytel 101 NC010, an unmodified semicrystalline nylon 6.8 polymer. The properties of this polymer are discussed elsewhere (24, 26). Three different carbon fillers were employed in this project. Akze Nobel Ketjenblack EC-600 JD. an electrically conductive carbon black, was used. The highly branched, high surface area carbon black structure allows it to contact a large amount of polymer, which results in improved electrical conductivity at low earbon black concentrations. Thermocarb™ TC-300 Specialty Graphite, a high purity synthetic graphite available from Conoco, Inc., was used because of its high thermal conductivity and moderately high electrical conductivity. The properties of these two fillers are discussed elsewhere (24, 27, 28). Akzo Nobel's Fortafil 243 PAN based 3.2 mm chopped and pelletized carbon fiber was used to improve the electrical and thermal conductivity and the tensile strength of the resin. Fortall 243 was surface treated and then formed into pellets. A proprietary polymer (sizing) is used as a binder for the peliets that also promotes adhesion with riylon. Table I shows the properties of this carbon fiber (29).

In this study, a 2³ factorial design (three factors or fillers in this case at two different loading levels) and a complete replicate was completed. For all fillers, the low loading level was 0 wt%. The high loading level varied for each filler. The high levels were 5 wt% for Ketjenblack EC-600 JD, 30 wt% for ThermocarbTM TC-300 Specialty Graphite, and 20 wt% for Fortafil 243. Table 2 shows the factorial design formulations. In Table 2, "CB" signifies carbon black, "SG" signifies synthetic graphite (ThermocarbTM TC-300 Specialty Graphite),

Table 1. Properties of Akzo Nobel Fortafil 243 PAN Based 3.2 mm Chopped and Pelletized Carbon Fiber (29).

Carbon Content	95 wt%
Electrical Resistivity	0.00167 ohm-cm
Thermal Conductivity	20. W/m-K (axial direction)
Tensile Strength	3800 MPa
Tensile Modulus	227 GPa
Specific Gravity	1.74 g/cm ³
Fiber Diameter	7.3 microns
Fiber Shape	Round
Fiber Mean Length	3.2 mm (entire range is 2.3 mm to 4.1 mm)
Binder Content	2.6 wt% proprietary polymer that adheres pellet together and promotes adhesion with nylon matrix
Bulk Density	356 g/l

and "CF" signifies earbon liber. Since this project tocuses on producing highly conductive composites, the high leading levels were chosen so that the filler amounts would be above the electrical conductivity percolation threshold. This percolation threshold is defined as the conductive filler concentration above which there is a sharp increase in composite electrical conductivity. Below this threshold, conductive particles are too far apart and no electrical conductivity occurs. Based on prior results, these percolation thresholds had already been determined (24, 30-32). Another consideration was that the total wi% filler for the composite with all fillers at the high level be 55 wt%. Higher filler amounts would likely make it difficult to extrude and injection mold the conductive resin into test specimeris.

Thermal conductivity was also measured on composites containing only one type of carbon filler in the type of these single filler composites are shown in Table 3.

Test Specimen Fabrication

For this entire project, the fillers were used as received. Zyiel 101 NC010 was dried in an indirect heated dehumidifying drying oven (dewpoint of the recirculating air = -40° C). After drying, the polymer was stored in moisture-barrier bags.

Table 2. Filler Loadings in Factorial Design Formulations for Nylon 6,6.

Formulation .	Ketjenblack EC-600 JD, wt%	Thermocarb™ TC-300 Specialty Graphite, wt%	Fortafil 243 Carbon Fiber, wt%
No filler	0	0	0
CB	5	0	0
SG	0	30	0
CB*SG	5	30	0
CF	Ö	0	20
CB*CF	5	0 .	20
SG*CF	0 .	. 30	20
CB*SG*CF	5	30	20

Table 3. Single Filler Loading Levels for Nylon 6,6.

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Filler	Loading Levels, wt%	
Kejenblack EC-600 JD	2.5, 4.0, 5.0, 6.0, 7.5, 10.0	
Thermocarb™ TC-300 Specialty Graphite	10.0, 15.0, 20.0, 30.0, 40.0	
Fortafil 243 Carbon Fiber	5.0, 7.0, 10.0, 15.0, 20.0, 30.0, 40.0	

The extruder used was an American Leistritz Exunder Corporation Model ZSE 27, which has a 27 mm co-rotating intermeshing twin screw with 10 zones and a length/diameter ratio of 40. The serew design was chosen to obtain the maximum possible conductivity; it is described in detail elsewhere (25). Hence, a minimum amount of filler degradation was desired. while still dispersing the fillers well in the polymer. The same screw design was used for this entire project. The Zytel polymer peliets were introduced in Zone 1. The first side stuffer, utilized to introduce carbon black and Thermocarban TC-300 Specialty Graphite into the polymer melt, was located at Zone 5. The second side stuffer was located at Zone 7 and was used to introduce the carbon fiber into the polymer melt. Four Schenck AccuRate gravimetric feeders were used to accurately conirol the amount of each material added to the extruder.

After passing through the extruder, the polymer strands (3 mm in diameter) entered a water bath and then a pelletizer that produced nominally 3 mm long pellets. After compounding, the pelletized composite resin was dried again and then stored in moisture barrier bags prior to injection molding.

A Niigata injection molding machine, model NESSUA, was used to produce test specimens. This machine has a 40 mm diameter single screw with a length/diameter ratio of 18. The lengths of the feed, compression, and metering sections of the single screw are 396 mm, 180 mm, and 144 mm, respectively. A four cavity mold was used to produce 6.4 cm diameter disks that are 3.2 mm thick. The thermal conductivity of all formulations were determined.

Through-Plane Thermal Conductivity Test Method

The through-plane thermal conductivity of a 3.2 mm thick, 5 cm diameter disc-shaped test specimen was measured at 55°C using a Holometrix Model TCA-300 Thermal Conductivity Analyzer, which uses ASTM F433 guarded heat flow meter method (33). The mylon 6.6 based samples were all tested dry as molded (DAM). For each formulation, at least 3 samples were tested.

Filler Longth and Aspect Ratio Test Method

in order to determine the length of the carbon fiber and synthetic graphite in the test specimens, solvent digestion was used. A 0.2 g sample cut from the center of a thermal conductivity specimen was dissolved at 23°C using formic acid to remove the nylon 6.6. The fillers were then dispersed onto a glass slide and viewed using an Olympus SZH10 optical microscope with an Optronics Engineering LX-750 video camera. The images (at 60× magnification) were collected using Scion Image version 1.62 software. The images were then processed using Adobe Photoshop 5.0 and the Image Processing Tool Kit version 3.0. The length and aspect ratio (length/diameter) of each filler was measured. For each formulation, between 1000 and 6000 particles/fibers were measured. Because of the extremely small size of the carbon black, the length and aspect ratio of the carbon black were not measured.

Filler Orientation Test Method

in order to determine the orientation of the carbon fillers, a polished composite sample was viewed using an optical microscope. Again, because of the small size of the carbon black (aggregates 30 to 100 nm in size), the orientations of only the synthetic graphite particles and carbon fibers were determined. Two 13 mm by 13 mm squares were cut from the center of each through-plane thermal conductivity sample, as shown in Fig. 1. These samples were cast in two-part epoxy plugs such that two different images (one exposes the through the sample thickness 3.2 mm face) could be viewed, as shown in Fig. 2. The samples were then polished and viewed using an Olympus BX60 reflected

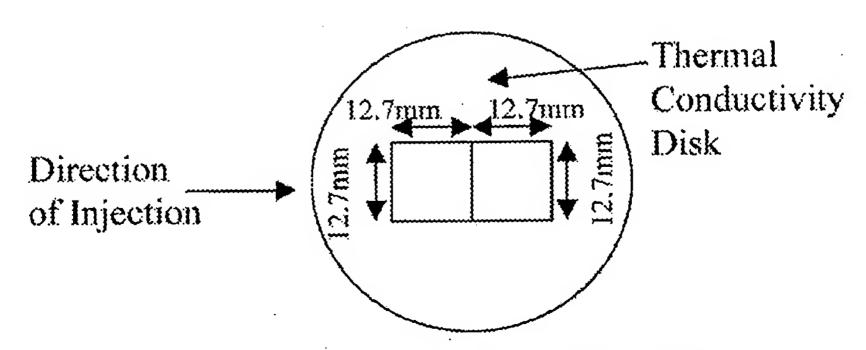


Fig. 1. Diagram showing location of image analysis specimens.

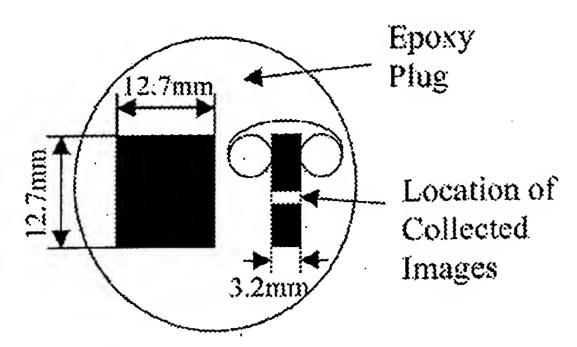


Fig. 2. Diagram showing where images collected on throughplane thermal conductivity samples.

light microscope at a magnification of 200×. Again, the images were collected using Scion Image version 1.62 software. The images were then processed using Adobe Photoshop 5.0 and the Image Processing Tool Kit version 3.0. For each formulation, the orientation was determined by viewing typically 1000 to 6000 particles/fibers.

RESULTS

Filler Length and Aspect Ratio Results

Table 4 shows the mean length and aspect ratio (length/diameter) results of the synthetic graphite particles and carbon fibers for the factorial design formulations after the fillers were removed via solvent digestion. The values listed under the "as received" formulation are the length and aspect ratio of the filler prior to extrusion and injection molding (34–36).

The results in Table 4 show there is significant degradation of the carbon fibers following the extrusion and injection molding steps. Prior to processing, the mean length of the carbon fibers is 3200 microns, with an aspect ratio (length/diameter) of 438. In the 20 wt% carbon fiber formulation in pylon 6.6, the fibers now have a mean length of 117 microns (aspect ratio = 16.0). In the nylon based composites containing both carbon fibers and synthetic graphite, the mean length

Table 4. Mean Length and Aspect Ratio Results for Factorial Design Formulations (34-36)

	Nylon 6,6	
Formulation	Length (μm)	Aspect Ratio
As Received Carbon Fibers (CF)	3,200.	438.36
As Received Synthetic Graphite (SG)	68.3	1.80
SG Only Composites	70.6	1.68
SG Only Replicate Composites	68.5	1.70
CF Only Composites	120.7	16.54
CF Only Replicate Composites	113.5	15 <i>.</i> 55
CF (SG*CF Composites)	110.5	15.14
SG (SG*CF Composites)	44.2	1.70
CF (SG*CF Replicate Composites)	106.2	14.55
SG (SG*CF Replicate Composites)	53.0	1.66

of the fibers was 108 microns (aspect ratio = 14.8). These length results are comparable to those reported by Bigg, which showed that carbon fiber/nylon 6.6 composites had fiber lengths of approximately 130 microns after extrusion and injection molding (37).

Table 4 also shows the lengths and aspect ratios of the synthetic graphite particles (Thermocarb TC-300 Specialty Graphite). Table 4 shows that the length and aspect ratio of the synthetic graphite particles in the composite specimens remain similar to those of the as received material. This result is likely due to the relatively small length and aspect ratio of the as received ThermocarbTM TC-300 Specialty Graphite. The as received synthetic graphite has a mean length of 68 microps and a mean aspect ratio of 1.8. In the 30 wt% synthetic graphite formulation in nylon 6.6, the graphite particles now have a mean length of 70 microns (aspect ratio = 1.69). In the nylon based composites containing both carbon fibers and synthetic graphite particles. the mean length of the synthetic graphite was 49 microns (aspeci, ratio = 1.68).

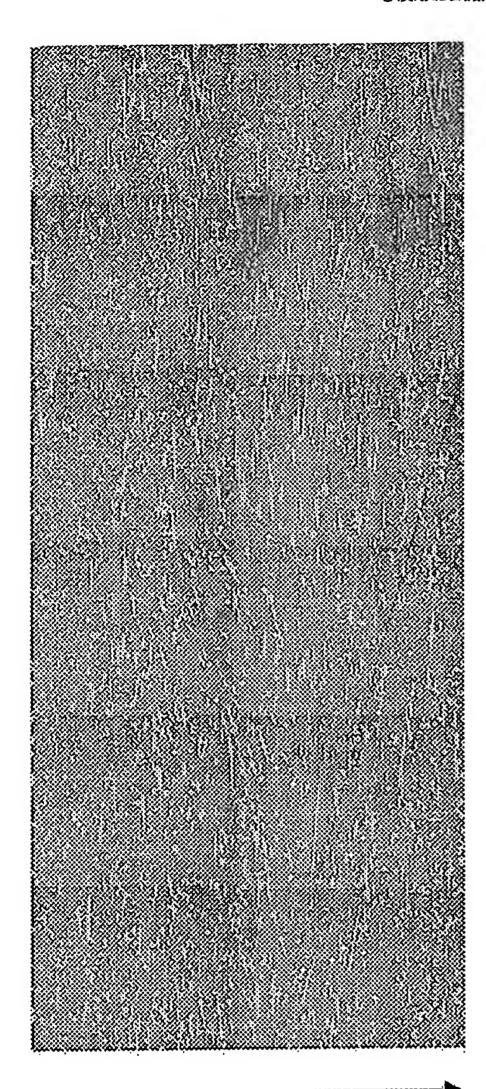
Filler Orientation Results

As discussed previously, the filler orientation angle was measured by optical microscopy. The angle of interest in these measurements was the deviation of the filler away from the thermal conductivity measurement direction. For these measurements, all the angles are between zero and 90°. An angle of zero degrees signifies that the particles/fibers are aligned parallel to the thermal conductivity measurement direction. An angle of 90° means that the filler is perpendicular to the thermal conductivity measurement direction.

For the sample containing 30 wt% Thermocarb™ TC-300 Specialty Graphite, the mean orientation angle was 58° with a standard deviation of 25° (3784 particies measured). A photomicrograph of a composite containing this filler is shown elsewhere (23). The mean orientation augle varied from 58° to 62° for all the composites containing Thermocarb™ TC-300 Specialty Graphite. For the composite containing 20 wi% Fortafil 243, the mean orientation angle was 65° with a standard deviation of 20° (1784 fibers measured). Figure 3 shows a photomicrograph at a magnification of 200× of the 20 wt% Fortafil 243 in nylon 6,6 throughplane thermal conductivity specimen. The arrow below Fig. 3 indicates the direction of thermal conductivity measurement. For all the composites containing Fortall 243, the mean orientation angle varied from 61° to 80°. Hence, the orientation angle is closer to 90°, indicating that the fibers/particles are primarily orientated transverse to the thermal conductivity measurement direction.

Through-Plane Thormal Conductivity Results

Figure 4 shows the through-plane thermal conductivity results for the composites containing only varying amounts of single fillers as a function of volume fraction. These formulations correspond to those shown



Direction of Conduction

Fig. 3. Through-plane thermal conductivity sample containing 20 wt% Fortafil 243 carbon fiber in nylon 6,6 at 200 × magnification.

in Table 3, which displays wi%. Each data point shown in Fig. 4 is the mean of 3 to 7 samples tested per formulation. The standard deviation was typically less than 5% of the mean.

Tigure 4 shows that carbon black does increase the TC of the polymer from 0.30 W/m·K for the pure nylon 6.6 to 0.45 W/m·K for the composites containing 10 wt% (6.6 vol%) carbon black. Composites containing Thermocarb™ TC-300 Specialty Graphite had the largest TC values. The composite containing 40 wi% (25.3 vol%) Thermocarb™ TC-300 Specialty Graphite in nylon had a TC value of 1.16 W/m·K. Adding 40 wt%

(29.5 vol%) carbon fiber to mylon produced a composite with a TC of 0.55 W/m·K.

tion, and number of samples tested) for each of the factorial design formulations in mylon 6,6. Since a complete replicate of the factorial design was completed, one column is labeled "original" and the other column is labeled "replicate." As stated previously. Table 2 defines the factorial design formulations. The results in Table 5 show a wide range of TC values. The highest TC result shown here is 1.9 W/m-K for the composite containing all 3 carbon fillers. Even though it appears that composites containing multiple fillers produce higher composite TC values, the exact effect of the combinations is not obvious without the application of statistical experimental design calculations.

Factorial Design Analysis: Through-Pinne Thermal Conductivity

Using the results shown in Table 5, an analysis of the factorial design was completed. This was performed using the Minitab version 1.3 Statistical Software package. For this analysis, the effects and T (sometimes designated t) and P (also called p) values for the TC results were calculated. Large T (refers to the Student-t distribution) values and small P (smallest level of significance that would lead to the rejection of the mult hypothesis) values indicate that a factor (filler in this case) may have a significant effect on the composite TC (38). For all statistical calculations, the 95% confidence level was used.

Factorial designs were used in the project since they are the most efficient type of experiment to determine the effect of each filler and any possible interactions between fillers. By using factorials, one can determine the effect that each factor (filler) has on the system by calculating a single value to quantify the change in TC as the amount of a filler is increased. These calculated effects can then be ranked to determine which fillers and combinations of fillers produced a larger change in TC values (38).

The effects, coefficients, and T and P values for the nylon 6,6 based composites are given in Table 6, showing the values for all of the filler combinations. Further investigation of Table 6 yields some important information regarding the effects that fillers have on conductivity. First, all the effect terms are positive, which indicates that the addition of any filler increases the thermal conductivity of the composite. Second, the effect term is the largest for the synthetic graphite (ThermocarbTM TC-300 Specialty Graphite), which indicates that synthetic graphite causes the largest increase in composite through-plane thermal conductivity. After synthetic graphite, the effect of the fillers follows the following order: carbon fiber, the combination of synthetic graphite and carbon fiber, carbon black, the combination of synthetic graphite and carbon black, the combination of all three fillers, and last the combination of carbon black and carbon fiber. All of the formulations are statistically significant at the

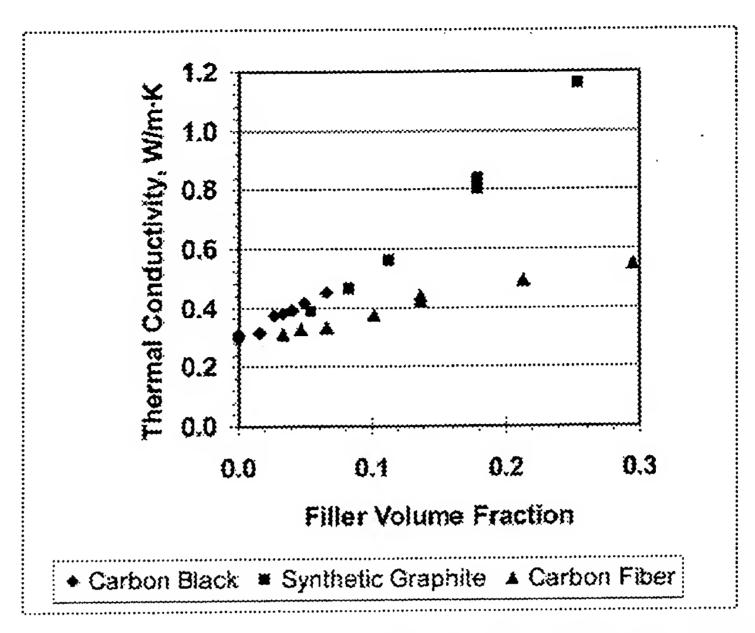


Fig. 4. Through-plane thermal conductivity results for composites containing single carbon fillers.

95% confidence level (P < 0.05). The statistically significant results for all the multiple filler cases show that there is an effect on TC when different fillers are combined. In this case, a statistically significant interaction term indicates that the composite TC is higher than what would be expected from the additive effect of each single filler (38). For example, the most significant interaction was that of synthetic graphite/carbon liber. This means that, for example, when synthetic graphtie and carbon fiber were combined and added to nylon, then the TC of the composite increased more than what would be expected from the individual additive effect of synthetic graphite and carbon liber. This result has been noticed in the past (23). It is likely that thermally conductive pathways are formed that "link" the highly branched, high surface area carbon black, carbon fiber, and synthetic graphite, which results in increased composite TC.

As stated previously, resins with a thermal conductivity of at least I W/m·K can be used in heat sink

Table 5. Through-Plane Thermal Conductivity Results for Factorial Design Formulations in Nylon 6,6 (23).

Formulation	Thermal Conductivity, W/m-K		
	Orlginal	Replicate	
No filler	0.297 ± 0.007 n = 4	$0.309 \pm 0.006 \text{n} = 4$	
CB	$0.381 \pm 0.003 \text{n} = 4$	$0.383 \pm 0.002 \text{n} = 4$	
SG	$0.802 \pm 0.050 \text{n} = 6$	$0.836 \pm 0.062 \text{n} = 6$	
CB*SG	$0.956 \pm 0.003 \text{n} = 4$	$0.999 \pm 0.072 \text{n} = 6$	
CF	$0.424^{\circ} \pm 0.015 \text{n} = 5$	$0.438 \pm 0.004 \text{n} = 4$	
CB*CF	$0.490 \pm 0.001 \text{n} = 4$	$0.494 \pm 0.002 \text{n} = 3$	
SG*CF	$1.536 \pm 0.019 n = 4$	$1.486 \pm 0.017 \text{n} = 4$	
CB*SG*CF	$1.843 \pm 0.039 \text{n} = 4$	$1.873 \pm 0.020 \text{ n} = 3$	

applications (I). In this study, the resins containing the combination of carbon black and synthetic graphite, the combination of synthetic graphite and Fortafil 243, and all three fillers had a TC of at least I W/m·K. Hence, these conductive resens could be used for heat sink applications.

A prior project investigated the effect on composite TC using this same nylon, carbon black, and synthetic graphite particles, but with a different carbon fiber. In this past project, BP/Amoco's milled (200 micron long) pitch based carbon fiber. ThermalGraph DKD X, was used (23). The axial thermal conductivity of ThermalGraph DKD X is 600 W/m·K versus 20 W/m·K for Fortafil 243 (23). Comparing the results from this present study to the previous one yields some interesting observations. In both studies for the through-plane thermal conductivity samples, the synthetic graphite particles and carbon fibers are mainly oriented transverse to the direction of thermal conductivity measurement. The length and aspect ratio of the composites containing Fortafil 243 were typically

Table 6. Factorial Design Analysis for Nylon 6,6 Based Conductive Resins.

Term	Effect	Coefficient	T	P
Constant		0.847	164.7	0.000
CB	0.161	0.081	15.7	0.000
SG	0.889	0.445	86.5	0.000
CF	0.452	0.226	44.0	0.000
CB*SG	0.091	0.046	8.9	0.000
CB*CF	0.043	0.021	4.2	0.003
SG*CF	0.334	0.167	32.5	0.000
CB*SG*CF	0.052	0.026	5.0	0.001

115 microns and 16, respectively. The length and aspect ratio of the composites containing ThermalGraph DKD X were hypically 100 microus and 10, respectively (39). Hence, the lengths and aspect ratios of both carbon fibers in the composite sample are similar.

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For the composites filled only with carbon fiber, the resins containing 20 wt% (11.7 vol%) ThermalGraph DKD X had a TC of 0.48 W/m-K as compared to 0.43 W/m-K for those containing 20 wt% (13.7 vol%) Fortafil 243. The TC value for the composites containing 20 wt% ThermalGraph DKO X along with 5 wt% carbon black was 0.57 W/m·K, which is similar to the TC value of 0.49 W/m-K for those containing 20 wt% Fortafil 243 and 5 wt% carbon black. The TC value for the composites containing 30 wt% synthetic graphite along with 20 wt% ThermalGraph DED X was 1.75 W/m-K versus the TC value of 1.51 W/m K for the 30 wt% synthetic graphite/20 wt% Fortaff 243 composites. The TC value for the composites containing all three different fillers (5 wt% carbon black, 30 wt% synthetic graphile, and 20 wi% carbon fiber) was 1.97 W/m-K (for Thermal-Graph D&D X) as compared to 1.86 W/m-K (for Fortafil 243). Thus, it appears that the higher thermal conductivity for the ThermalCraph DKD X does not translate into a greatly superior composite TC.

When considering the current and prior factorial design thermal conductivity results, the most significant effects for these resins were synthetic graphite, followed by carbon fiber, then the combination of synthetic graphite and carbon fiber, and then carbon black (23). This once again shows that when the higher thermal conductivity ThermalGraph DRD X is used in a composite material, the composite thermal conductivity is similar to that obtained by using Fortafil 243.

Another difference between the two carbon fibers is that Fortafil 243 was surface treated to improve adhesion to mylon. ThermalGraph DKD X was not surface treated (23, 25, 34). Tensile results for composites containing each of these carbon fibers suggests that the adhesion of Fortafil 243 to the matrix is higher than the ThermalCraph DKD X-matrix adhesion (40). For example, the ultimate tensile strength was 97.7 MPa for the composite containing only 20 wt% (11.7 vol%) ThermalGraph DKD X (composite TC = 0.48 W/m·K). The ultimate tensile strength was 196 MPa for the composite containing only 20 wt% (13.7 vol%) Fortafil 243 (composite TC = 0.43 W/m-K). These tensile results suggest that the apparent improved adhesion for the Fortafil 243 carbon fiber with the matrix material did not dramatically increase composite through-plane thermal conductivity.

CONCLUSIONS

As a result of this study, the following conclusions can be made concerning the filler length, aspect ratio, and orientation. Extrusion and injection molding reduced the length of the carbon fiber in the conductive composites from approximately \$200 microns to 115 microns and reduced the aspect ratio from 438 to 16.

However, the length (typically 60 to 70 microns) and aspect ratio (typically 1.7 to 1.8) of the ThermocarbTM TC-300 Specialty Graphite in the composite specimens remain similar to those of the as received material. This high purity synthetic graphite likely maintained its size better than carbon fiber since the as received ThermocarbTM material has a smaller length and aspect ratio. Concerning orientation, for the through-plane thermal conductivity samples, the synthetic graphite particles and carbon fibers are mainly oriented transverse to the direction of thermal conductivity measurement.

Considering only the through-plane thermal conductivity of composites containing a varying amount of a single filler. ThermocarbTM TC-300 Specialty Graphite caused the largest increase in composite throughplane thermal conductivity. The thermal conductivity increased from 0.3 W/m·K (pure polymer) to 1.16 W/m·K for the composites containing 40 wt% (25.3 vol%) ThermocarbTM TC-300 Specialty Graphite.

By studying the though-plane thermal conductivity factorial experiment results, the fillers can be ranked in the order shown below:

ThermocarbTM TC-300 Specialty Graphite > Fortafil 243 Carbon Fiber > ThermocarbTM TC-300 Specialty Graphite/Fortafil 243 Carbon Fiber Combination > Carbon Black > Carbon Black/ThermocarbTM TC-300 Specialty Graphite Combination > Carbon Black/ThermocarbTM TC-300 Specialty Graphite/Fortafil 243 Carbon Fiber Combination > Carbon Black/Fortafil 243 Carbon Fiber Combination.

Hence, Thermocarb™ TC-300 Specialty Graphite caused the largest increase in composite through-plane thermal conductivity. Another important result is that all the single fillers and combinations of fillers caused a statistically significant increase in composite thermal conductivity. It is likely that thermally conductive pathways are formed that "link" the high surface area carbon black, carbon fiber, and the synthetic graphite particles, which results in increased composite thermal conductivity.

In this study, the resius containing the combination of carbon black and synthetic graphite, the combination of synthetic graphite and Fortafil 243, and all three fillers had a TC of at least 1 W/m·K. Hence, these conductive resins could be used for heat sink applications.

A prior project investigated the effect on composite TC using this same rylon, carbon black, and synthetic graphite particles, but with a different carbon liber. In this past project, BP/Amoco's milled (200 micron long) pitch based carbon fiber, ThermalGraph DKD X, was used (23). This carbon fiber has an axial thermal conductivity of 600 W/m·K versus 20 W/m·K for Fortafil 243. When comparing the results of this current study with one previously conducted, it was observed that the through-plane thermal conductivity was similar for the factorial design formulations regardless of the carbon fiber used.

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REFERENCES

- J. M. Finan, "Thermally Conductive Thermoplastic Materials," Proceedings of Society of Plastics Engineers' Annual Technical Conference, 1547 (May 1999).
- 2. Y. Agari and T. J. Uno, J. Appl. Polym. Sci., 30, 2225 (1985).
- 3. D. M. Bigg, Polym. Eng. Sci., 17, 842 (1977).
- 4. D M Bigg. Adv. Polym. Technol., 4, 255 (1984).
- M. Narkis, G. Lidor, A. Vaxman, and L. Zuri, J. Electrost., 47, 201 (1999).
- 6. K. Nagata, H. Iwabuki, and H. Nigo, Compos. Interfaces, 8(5), 483 (1999).
- A. Demain, "Thermal Conductivity of Polymer-Chopped Carbon Fibre Composites," Ph.D. Dissertation, Universite Catholique de Louvain, Louvain-la-Neuve, Belgium (1994).
- 8. J. A. King, K. W. Tucker, J. D. Meyers, E. A. Weber, M. L. Clingerman, and K. R. Ambrosius, Polym. Compos., 22, 142 (2001).
- M. V. Murchy, Proceedings of the Society of Flastics Engineers' Annual Technical Conference, 1396 (1994).
- R. M. Simon, Pohjm. News. 11, 102 (1985).
- P. Mapleston, Mod. Plast., 69, 80 (1992).
 D. M. Bigg, Polym. Compos., 7, 125 (1986).
- 13. J.-P. Issi, B. Nysten, A. Jonas, A. Demain, L. Piraux, and B. Poulaeri, "Tailoring the Thermal Conductivity of Organic Materials," in *Thermal Conductivity* 21, p. 629. Edited by C. J. Cremers and H. A. Fine, Plenum Press,
- New York (1990). 14. L. E. Nielsen, Ind. Eng. Chem. Fundam., 13, 17 (1974).
- A. Demain and J.-P. Issi, J. Compos. Mater., 27, 668 (1993).
- 16. B. Nysten and J.-P. Issi, Composites. 21, 339 (1990).
- 17. B. Nysten, A. Jonas, and J.-P. Issi, "Effect of Carbon Fibers Length on the Low Temperature Thermal Conductivity of a Thermoplastic Composite," in *Thermal Conduc*tivity 21, p. 647, Edited by C. J. Cremers and H. A. Fine, Plenum Press, New York (1990).
- 18. J.-P. Issi and B. Nysten, "Electrical and Thermal Transport in Carbon Fibers," in Carbon Fibers, 3rd Edition, Chap. 6. Edited by J. B. Donnet, S. Rebouillat, T. K. Wang, and J. C. M. Peng, Marcel Dekker Inc., New York (1908)
- 19. B. Erosius, High Performance Composites, "Fitch Fibers Take the Heat Out," 22-28, (September/October 2001).

- 20. J.-B. Donnet, R. C. Bansal, and M.-J. Wang, Carbon Black, 2nd Edition, Marcel Dekker, Inc., New York (1993).
- 21. R. Taipalus, T. Harmia, M. Q. Zhang, and K. Friedrich. Compos. Sci. & Tech., 61, 801 (2001).
- 22. W. Thongruang, R. J. Spentak, and C. M. Balik, Polymer, 43, 3717 (2002).
- 23. E. H. Weber, M. L. Clingerman, and J. A. King, J. Appl. Polym. Sci. 88, 112 (2003).
- 24. M. L. Clingerman, E. H. Weber, and J. A. King. Polym. Compos., 23. 911 (2002).
- 25. Q. Krueger and J. A. King, Adv. Polym. Technol. 22(2) (2003).
- 26. DuPont Zytel Nylon Resin Product and Properties. DuPont Engineering Polymers, Version 95.9, Wilmington, DE.
- 27. Akzo Nobel Electrically Conductive Ketjenblack Product Literature, 300 S. Riverside Plaza, Chicago, IL, 60606 (1999).
- Conoco Carbon Products Product Literature, Conoco Inc., P.O. Box 2197, Houston, TX 77252-2197 (1999).
- Akzo Nobel Fortafii Carbon Fibers Technical Data Sheet
 931B. Rockwood, TN 37854 (1993).
- M. L. Clingerman, E. H. Weber, J. A. King, and K. H. Schulz, J. Appl. Polym. Sci., 88, 2280 (2003).
- M. L. Clingerman, J. A. King, K. H. Schulz, and J. D. Meyers, J. Appl. Polym. Sci., 83, 1341 (2002)
- 32. M. L. Clingerman, J. P. Konell, E. H. Weber, J. A. King, and K. H. Schulz, "Comparison of Electrical, Thermal, and Mechanical Properties of Carbon Filled Resins," Proceedings of Society of Plastics Engineers' Annual Technical Conference, 1364 (May 2001).
- 33. "Evaluating Thermal Conductivity of Gasket Materials." ASIM Standard F 433-77 Reapproved 1993. American Society for Testing and Materials. Philadelphia. Pennsylvania (1996).
- 34. M. L. Clingerman, "Development and Modelling of Electrically Conductive Composite Materials," Ph.D. Dissertation, Michigan Technological University, Hougiston, Mi (2001)
- E. H. Weber. "Development and Modeling of Thermally Conductive Polymer/Carbon Composites." Ph.D. Dissertation. Michigan Technological University. Hougiston. Mi (2001)
- J. P. Konell, "Characterization and Tensile Modulus Modeling of Conductive Resins," Ph.D. Dissertation, Michigan Technological University, Houghton, MI (2002).
- 37. D. M. Bigg, Polym. Compos., 6, 20 (1985).
- 38. D. C. Montgomery. Design and Analysis of Experiments, 5th Edition, John Wiley & Sons, Inc., New York (2001).
- 99. J. P. Konell, J. A. King, and I. Miskingha. Polym. Composi, this issue, p. 172.
- J. A. Helser, J. A. King, J. P. Konell, I. Miskioglu, and L. L. Suiter, J. Appl. Polym. Sci., 91(5) (2004).